Heterogeneous & Homogeneous & Bio- & Nano-
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CATALYSIS

Supporting Information

Pillared Sn-MWW Prepared by a Solid-State-Exchange Method and its Use as a Lewis Acid Catalyst

Limin Ren[+],[a] Qiang Guo[+],[a] Marat Orazov,[b] Dandan Xu,[a] Dorothea Politi,[d] Prashant Kumar,[a] Saeed M. Alhassan,[c] K. Andre Mkhoyan,[a] Dimitrios Sidiras,[d] Mark E. Davis,[b] and Michael Tsapatsis*[a]

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Supporting Information

Synthesis of B-MWW: The boron MWW (MWW type borosilicate, ERB-1) layered precursor with a Si/B ratio of 13 was synthesized according to a literature method.[S1] In a typical run, 8.038 g of boric acid (> 99 %, Macron Chemicals) were dissolved into 68.4 g of distilled water. After stirring for 0.5 hour, 23.842 g of piperidine (99 %, Aldrich) were added to the solution and stirred for 0.5 hour. Then 12 g of fumed silica (Cab-o-sil M5) were added to the above solution. After stirring overnight, the gel with chemical composition $1SiO_2$: $0.65H_3BO_3$: 1.4piperidine: $19H_2O$ was transferred to autoclaves and hydrothermally treated in a rotation oven at 170 °C for 7 days. The products were separated and fully washed by filtration followed by drying at 70 °C overnight. The as-synthesized sample was denoted as B-MWW(Pr). Calcination of this sample was performed in static air at 580 °C for 10 hours. The calcined sample was denoted as B-MWW(3D).

Swelling and pillaring of B-MWW:

Swelling was performed by preparing a mixture with chemical composition $1SiO_2$: 0.18TPAOH: 1CTAB: $71.33H_2O$, where SiO_2 corresponds to the amount of SiO_2 contained in the B-MWW precursor (B-MWW(Pr)). As a typical run, 4 g of B-MWW(Pr) was mixed with 71 g of distilled water in a polypropylene bottle. After 15 minutes stirring, 22.47 g of cetyltrimethylammonium bromide (CTAB, > 99 %, Amresco) were added into the mixture and stirred for 15 minutes. Then 6.1 g of tetrapropylammonium hydroxide solution (TPAOH, 40 wt%, SACHEM) were added under stirring. After all the chemicals were mixed, the slurry was stirred at room temperature for 22 hours. Products were recovered by repeated cycles of centrifugation and washing (10 min centrifugation at 10 000 rpm). Pillaring of the swollen material was performed according to the literature.[S2] Typically, 1.0 g of swollen B-MWW powder was mixed with 6.5 g of tetraethoxysilane (TEOS, 98 %, Aldrich), after purging with argon gas for 10 minutes, the mixture was stirred for 25 h at 78 °C then filtered and dried at room temperature. The dried solid was hydrolyzed with a NaOH aqueous solution (pH = 8) for 6 h at 40 °C, and then filtered, dried at room temperature, and calcined in static air at 580 °C for 10 hours. The obtained product was noted as B-MWW(SP), where SP means swollen and pillared.

De-Boronation of B-MWW(SP):

De-Boronation was performed by 6M HNO_3 (1 g sample/50 mL 6M HNO_3) at 100 °C under refluxing. The procedure was performed twice. After acid treatment, products were collected by filtering and washed with distilled water. Then the sample was dried at 70 °C overnight. The obtained product was noted as De-B-MWW(SP).

SSE method for Sn insertion:

The solid-state-exchange (SSE) method was modified from the procedure reported by Hermans et al.[S3] 1 g of De-B-

MWW(SP) was ground with 0.0477 g of tin tetrachloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 98 %, Sigma-Aldrich) in a mortar for 15 minutes. Then the powders were calcined in the static air at 580 °C for 10 hours. The obtained product was noted as Sn-MWW(SP)-SSE.

Synthesis of Sn-MWW(3D): Sn-MWW precursor (Sn-MWW(Pr)) was synthesized by modifying the literature method.[S4] Here, the hydrothermal treatment time was prolonged from 5 days to 14 days. First, B-MWW(Pr) was deboronated by 6M HNO_3 (1 g zeolite/ 50 mL HNO_3) at 100 °C under reflux for 1 day, this procedure was performed twice. Then 2.5 g of the De-Boronated sample were mixed with 30 g of distilled water and 3.549 g of piperidine (99 %, Aldrich). After stirring for 1 hour, 0.146 g of tin tetrachloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 98 %, Aldrich) were added into the above mixture and stirred for 2 hours. Then the final gel with chemical composition $1SiO_2$: 0.01 SnO_2: 1.0piperidine: $40H_2O$ was transferred to an autoclave and hydrothermally treated in a rotation oven at 170 °C for 14 days. The products were separated and fully washed by filtration and then dried at 70 °C overnight. Calcination of this sample was performed in static air at 580 °C for 10 hours. The calcined sample was denoted as Sn-MWW(3D).

Sn-BEA Fluoride hydrothermal synthetic method: Sn-BEA zeolite was synthesized according to a literature method.[S5] First, 30.612 g of tetraethyl orthosilicate (TEOS, 98 %, Sigma-Aldrich) were mixed with 33 g of tetraethylammonium hydroxide solution (TEAOH, 35 wt%, SACHEM) and stirred for 1 hour. A clear solution of 0.412 g of tin tetrachloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 98 %, Sigma-Aldrich) in 2.75 g of water was added into the above mixture and stirred overnight to fully evaporate the ethanol. Then 3.143 g of hydrofluoric acid (HF 48-51 wt% in H_2O, Sigma-Aldrich) was added under stirring followed by adding a dealuminated BEA seeds suspension (0.36 g seeds in 1.75 g water). After manually mixing for 5 minutes, the final gel with a chemical composition $0.008SnO_2$: $1SiO_2$: 0.54TEAOH : 0.54HF : $10.6H_2O$ was transferred to autoclaves and hydrothermally treated in a rotation oven at 140 °C for 21 days. The products were separated and fully washed by filtration followed by drying at 70 °C overnight. After calcination at 600 °C in the static air condition for 6 hours, the final product was obtained and noted as Sn-BEA-F.

Synthesis of Sn-MFI: Sn-MFI zeolite was synthesized according to a literature method.[S6] First, 0.21 g of tin tetrachloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 98 %, Sigma-Aldrich) was dissolved into 5 g of distilled water. After stirring for 30 minutes, the solution was added to 15.612 g of tetraethyl orthosilicate (TEOS, 98 %, Sigma-Aldrich). Then 16.5 g of tetrapropylammonium hydroxide solution (TPAOH, 40 wt%, SACHEM) and 30.5 g water were added. After mixing for 5 hours the final gel with a chemical composition $0.008SnO_2$: $1SiO_2$: 0.44TPAOH : $34.36H_2O$ was transferred to autoclaves and hydrothermally treated in a static oven at 160 °C for 2 days. The products were separated and fully washed by filtration followed by drying at 70 °C overnight, then calcined at 550 °C in the static air for 6 hours.

Synthesis of Sn-SPP: Sn-SPP was synthesized as follows: 0.129 g of tin tetrachloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 98 %, Sigma-Aldrich) was dissolved into 7.35 g of tetra(n-butyl)phosphonium hydroxide (TBPOH, 40 wt%, TCI America) followed by the addition of 7.5 g of tetraethyl orthosilicate (TEOS, 98 %, Sigma-Aldrich). After hydrolysis, 3.2 g of deionized water was added to the mixture. The mixture was stirred overnight, and a clear sol was obtained. The

composition of the final sol is: 1.0SiO_2 : 0.03TBPOH : 4.0EtOH : 30H_2O : 0.01SnO_2. The sol was sealed in a Teflon-lined stainless steel autoclave and hydrothermally treated in a pre-heated static oven at 115 °C for 5 days. The solid products were centrifuged, washed with distilled water and then dried at 70 °C overnight and calcined at 823 K for 6 h in air under static conditions. The calcined samples were washed with water, dried at 343 K overnight and calcined at 823 K for 6 h in air under static conditions and this process was repeated to ensure removal of P_2O_5.

Characterization:

Powder X-ray diffraction (XRD) patterns were collected on a BrukerAXS D5005 diffractometer using Cu Kα radiation (λ=1.5418 Å). Data were collected in the 2θ range from 1 ° to 30 ° with a step size of 0.02 ° and a step time of 4 s. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) was used for elemental analysis. Samples were analyzed on a Thermo Scientific iCAP 6500 duo optical emission spectrometer fitted with a simultaneous charge induction detector. For each sample, standard and blank, the data were replicated 5 times to determine a mean and standard deviation for each selected elemental wavelength. SEM was performed on a JEOL JSM-6500F scanning microscope operated at 2 kV. TEM imaging was performed on an FEI Tecnai G 2 F30 TEM operating at 300 kV. All TEM images were captured using a CCD camera. Argon (-186 °C) adsorption was performed using a commercially available automatic manometric sorption analyzer (Quantachrome Instruments AutosorbiQ MP). Prior to adsorption measurements, the samples were outgassed at 300 °C for 5 h under turbomolecular pump vacuum. Full micro- and mesopore size distributions were calculated from the argon isotherms using the argon on zeolites/silica cylindrical pore adsorption branch method.[S7] FTIR spectra were recorded on a Thermo Scientific Nicolet iS50 FT-IR spectrometer with a built-in diamond attenuated total reflection (ATR) and acquired in the range of 4000-650 cm^{-1} and averaged over 16 scans. The data analysis was performed using Omnic software. The Diffuse Reflectance UV/Vis (DR-UV)spectra were recorded using Evolution 201/220 UV/Visible Spectrophotometers (Thermo Scientific) equipped with a diffuse reflectance cell. De-B-MWW was used as a background sample. Each collected spectrum was converted to Kubelka-Munk units mode. Kubelka-Munk function is the counterpart of the absorbance function and relates intensities directly to concentration, it is recommended to report DR-UV spectra in these units.[S8] Deuterated acetonitrile dosing and desorption experiments were performed using a Nicolet Nexus 470 Fourier transform infrared (FTIR) spectrometer with a Hg-Cd-Te (MCT) detector. Self-supporting wafers (10-20 mg/cm^2) were pressed and sealed in a heatable quartz vacuum cell with removable KBr windows. The cell was purged with air (1 cm^3/s, Air Liquide, breathing grade) while heating to 500 °C (1 °C /min), where it was held for 2 h, followed by evacuation at 500 °C for >2 h (<0.01 Pa dynamic vacuum; oil diffusion pump), and cooling to 35 °C under dynamic vacuum. At this point, a baseline spectrum was recorded. CD_3CN (Sigma-Aldrich, 99.8 % D-atoms) was degassed by three freeze (-196 °C), pump, thaw cycles, then dosed to the sample at 35 °C until the surface was saturated and physisorbed acetonitrile was observed. The cell was evacuated down to 13.3 Pa, and the first spectrum in each desorption series was recorded. Then, the cell was evacuated under dynamic vacuum while maintaining the sample at 35 °C. Concurrently, a series of representative FTIR spectra was recorded. The corresponding baseline spectrum was subtracted from each collected spectrum. Pyridine dosing and desorption experiments were performed in a similar manner on new catalyst pellets. Prior to dosing, baseline spectra were recorded at each temperature (35, 100, 200, and 350 °C). After adsorption,

pyridine was desorbed under dynamic vacuum at each temperature for 1 h prior to spectrum acquisition. The IR cell was heated at a rate of 5 °C /min to reach the next temperature in the program. Liquid ^{13}C NMR spectra were acquired in D_2O solvent on a Varian 500 MHz spectrometer equipped with an auto-x pfg broadband probe.

Catalytic reactions:

Baeyer-Villiger oxidation

Baeyer-Villiger oxidation of 2-adamantanone was performed on different tin-containing catalysts with reaction conditions: 1 mmol of 2-adamantanone (> 98 %, TCI) was dissolved into 3.09 g of dioxane (ACS grade, Millipore). Then 1.5 mmol of H_2O_2 (30 wt%, Fisher Scientific) and 100 µl of decane (as internal standard, > 99 %, Assay) were added to the solution. After mixing for 1 minute at room temperature, catalyst was added with a Sn/ketone ratio of 0.66 %. The reaction was performed at a 90 °C oil bath for 4 hours in a 20 mL thick walled glass vial (VWR). Needle syringe was used for sampling. For each point, the reaction bottle was quenched by ice water, and 0.2 ml of reaction solution was filtered into a small vial. 0.5 µl of sample was analyzed by gas chromatography (Agilent 6890A, Model# G1540A) equipped with a HP-5 column and a flame ionization detector.

The conversion and yield was calculated based on the total amount of starting ketone.

Conversion = (moles of ketone converted) / (initial moles of ketone) × 100 %.

Yield = (moles of lactone produced) / (initial moles of ketone) × 100 %.

Selectivity= (moles of lactone produced)/ (moles of ketone converted) × 100 %.

Mono and disaccharide isomerization

Reactions with mono and disaccharide were carried out in stirred 20-mL thick-walled glass reactors (VWR) sealed with crimp tops (PTFE/silicone septum, VWR). All the reactants and products were analyzed by high performance liquid chromatography (HPLC) using a refractive index detector with a Bio-Rad Aminex HPX87C (300 x 7.8 mm) column (Phenomenex). The mobile phase was ultrapure water (pH=7) and the column temperature was 80 °C.

Glucose isomerization

In a typical reaction with D-glucose (Sigma-Aldrich, ≥99.5 %), 0.05 g of glucose, 4.95 g of ethanol (1 wt% glucose in ethanol solution) and Sn containing catalyst (glucose/Sn=74) were added into the reactor and sealed. The reactor was placed in a temperature-controlled oil bath at 90 °C for a certain period of time. After quenching the reactor in an ice bath, 6.45 g of deionized water was added to hydrolyze the ethylated sugars at 90 °C for 24 h (before hydrolysis, the catalysts were filtered). The fructose yields listed in this manuscript are those obtained after the indicated reaction time and the 24 h hydrolysis.

Two types of isotopic tracing experiments were performed: isomerization of D-[^{13}C1;^{1}H2]-glucose (Omicron Bio, 99 % purity, 99 % ^{13}C enrichment) in CD_3OD, and isomerization of D-[^{13}C1;^{2}H2]-glucose in CH_3OD (Omicron Bio, 99 % purity, 99 % ^{13}C enrichment, 98 % ^{2}H enrichment). Both types of experiments were performed with 0.03 g of glucose, 2.97 g of corresponding solvent (1 wt% glucose in methanol solution) and Sn containing catalysts (glucose/Sn=74) were added into the reactor and sealed. The reactor was placed in a temperature-controlled oil bath at 90 °C for a certain

period of time. After quenching the reactor in an ice bath, the reaction solution was filtered, and the methanol was evaporated. 1.00 g of D_2O was added, and the ketals were hydrolyzed at 90 °C for 24 h. The resulting solution was analyzed by NMR without further treatment.

The conversion and yield was calculated based on the total amount of starting glucose.

Conversion = (moles of glucose converted) / (initial moles of glucose) × 100 %.

Fructose Yield = (moles of fructose produced) / (initial moles of glucose) × 100 %.

Fructose Selectivity= (moles of fructose produced)/ (moles of glucose converted) × 100 %.

Mannose Yield = (moles of mannose produced) / (initial moles of glucose) × 100 %.

Fructose Selectivity= (moles of mannose produced)/ (moles of glucose converted) × 100 %.

Long term stability test was performed by running reaction over recycled and calcined catalyst. After the first 8 h glucose isomerization, catalyst was separated and washed by centrifuging with methanol. After drying, the recycled sample was calcined at 550 °C with static air for 4h. Then the calcined sample was used as catalyst for the next 8h reaction. After each run, sample recycling was performed in the same way. Totally, 5 cycles of 8h reaction were performed.

Maltose isomerization

Reactions with maltose (Maltose Monohydrate (Sigma-Aldrich, ≥ 99.5 %)) were carried out in ethanol or n-propanol (1 wt% maltose in 3 g of alcohol solution) at a 1:35 Sn/maltose molar ratio in stirred 20-mL thick-walled glass reactors. The reactor was placed in a temperature-controlled oil bath at 90 °C for a certain period of time. After quenching the reactor in an ice bath, 4 g of deionized water was added to perform the hydrolysis (before hydrolysis, the catalysts are filtered) at 90 °C for 48 h. The maltulose yields plotted in this manuscript are those obtained after the indicated reaction time and the 48 h hydrolysis.

The conversion and yield was calculated based on the total amount of starting maltose.

Conversion = (moles of maltose converted) / (initial moles of maltose) × 100 %.

Maltulose Yield = (moles of maltulose produced) / (initial moles of maltose) × 100 %.

Maltulose Selectivity= (moles of maltulose produced)/ (moles of maltose converted) × 100 %.

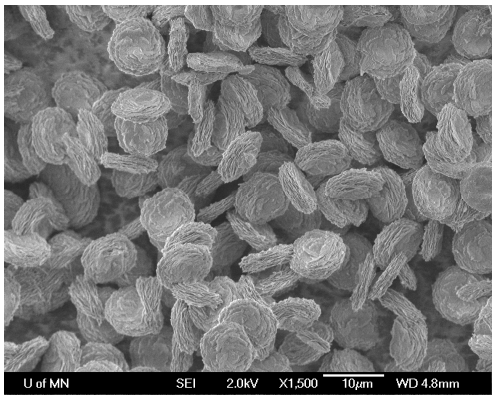


Figure S1. SEM image of B-MWW(Pr).

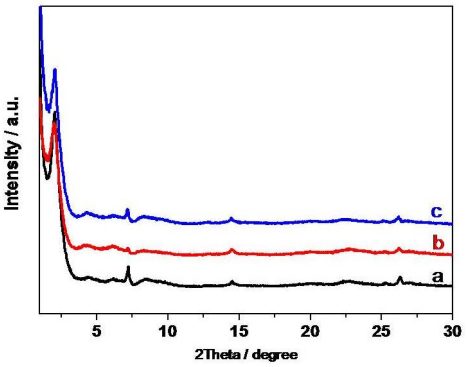


Figure S2. XRD patterns of B-MWW(SP) (trace a), De-B-MWW(SP) (trace b) and Sn-MWW(SP)-SSE (trace c).

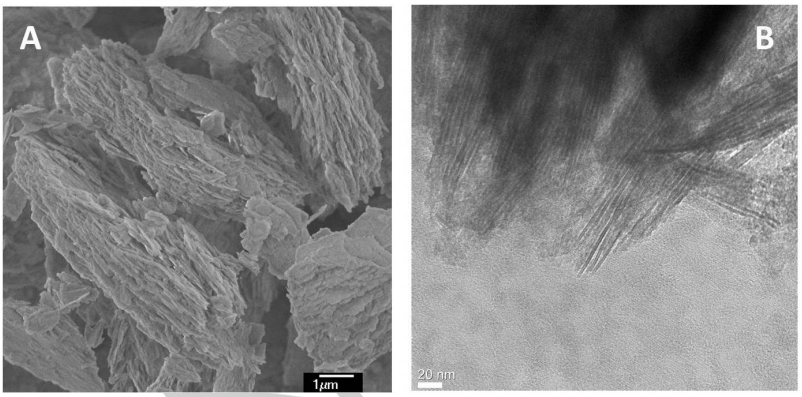


Figure S3. A). SEM and B). TEM images of Sn-MWW(SP)-SSE.

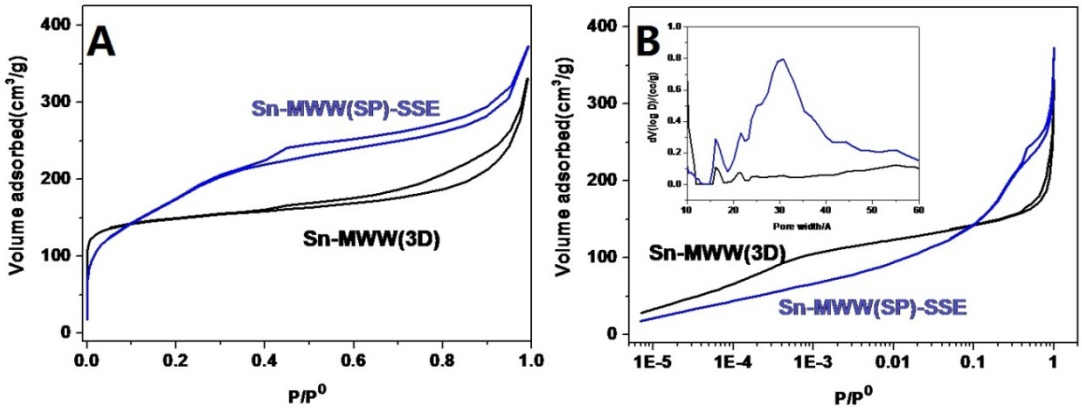


Figure S4. Ar adsorption-desorption isotherms plotted in A). linear mode and B). log mode (Inset shows pore size distribution obtained using NLDFT[S7]) of B-MWW(3D) and Sn-MWW(SP)-SSE.

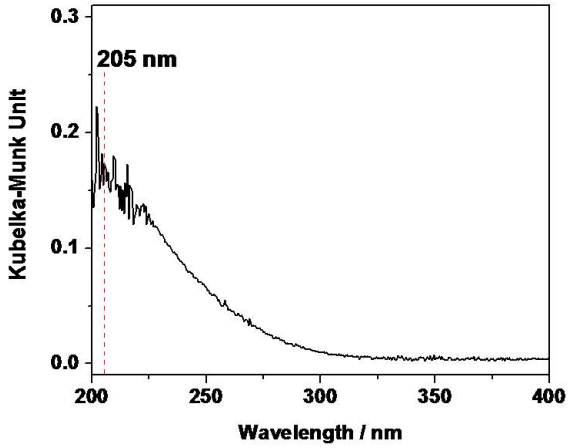


Figure S5. Diffuse Reflectance UV-visible spectrum of Sn-MWW(SP)-SSE.

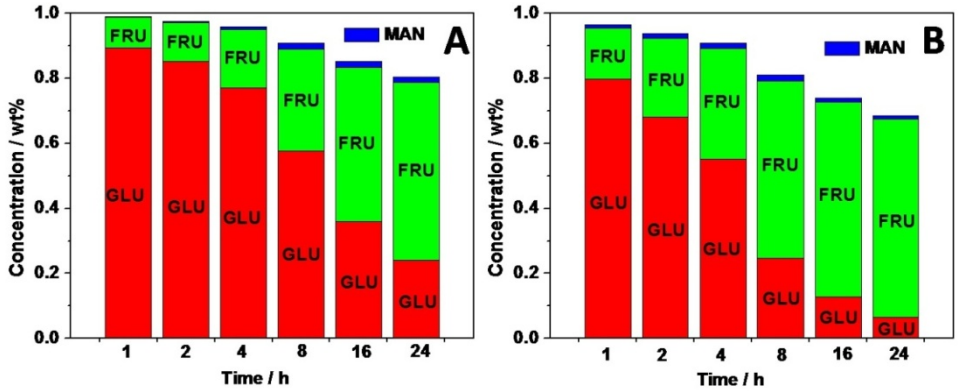


Figure S6. GLU isomerization reaction products distribution as a function of time. A: Sn-MWW(3D) and B: Sn-MWW(SP)-SSE as catalyst. Reaction conditions: 1 wt% GLU (0.05 g) in ethanol (4.95 g), GLU/Sn=74, 90 °C. After quenching the reactor in an ice bath, 6.45 g of deionized water was added to hydrolyze the ethylated sugars at 90 °C for 24 h. The fructose and mannose concentrations are obtained after the indicated reaction time and the 24 h hydrolysis. Reaction time is the time for reaction in ethanol before the addition of water. GLU, FRU and MAN stand for glucose, fructose and mannose, respectively.

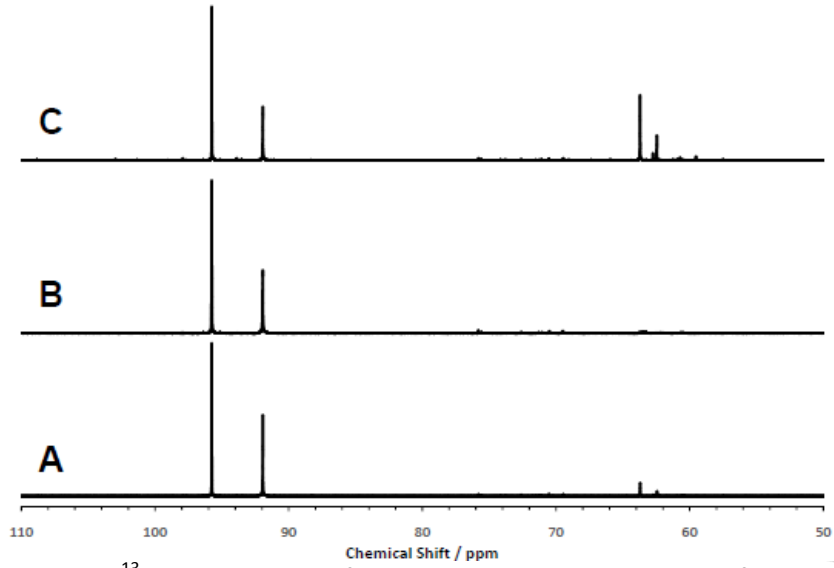


Figure S7. ^{13}C NMR spectra of hydrolyzed products obtained after reactions of A: D-[$^{13}C1$;$^{1}H2$]-glucose in CD_3OD catalyzed by Sn-MWW(SP)-SSE (2h); B: D-[$^{13}C1$;$^{2}H2$]-glucose in CH_3OH catalyzed by Sn-MWW(SP)-SSE (4h); C: D-[$^{13}C1$;$^{1}H2$]-glucose in CD_3OD catalyzed by Sn-MWW(3D) (6h).

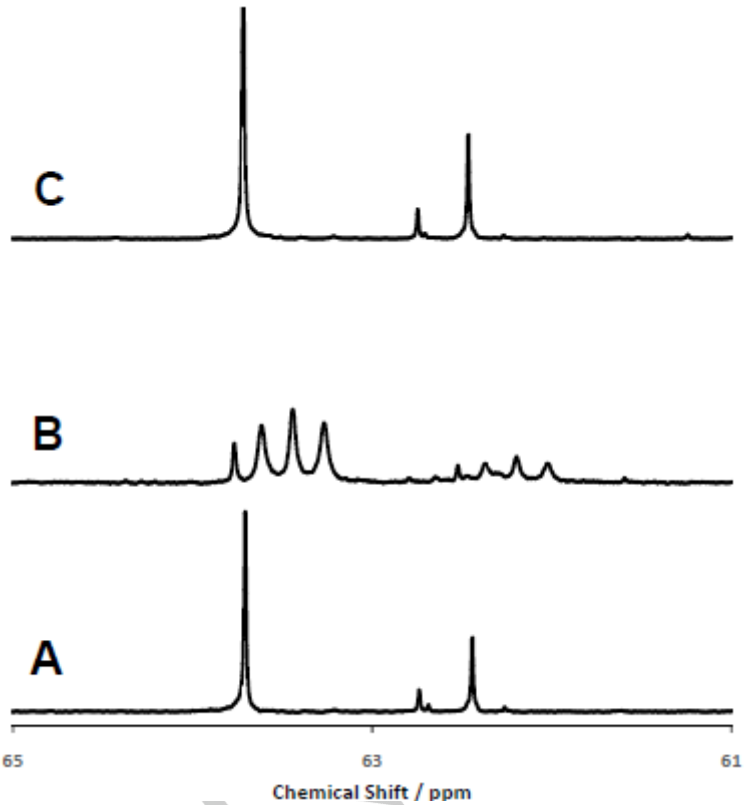


Figure S8. Zoomed in spectra (Ax11; Bx30; Cx3) from Figures S7, showing the fructose-C1 region. Lack of isotopic scrambling is inferred from all experiments. The small 63.7 ppm peak apparent in spectrum B next to the deuterium-split triplet is likely due to the 2 % $^{1}H2$ remaining in D-[$^{13}C1$;$^{2}H2$]-glucose. Nuclear Overhauser effect (NOE) leads to enhancement of signals from ^{1}H-bearing carbons, relative to ^{2}H-bearing carbons.

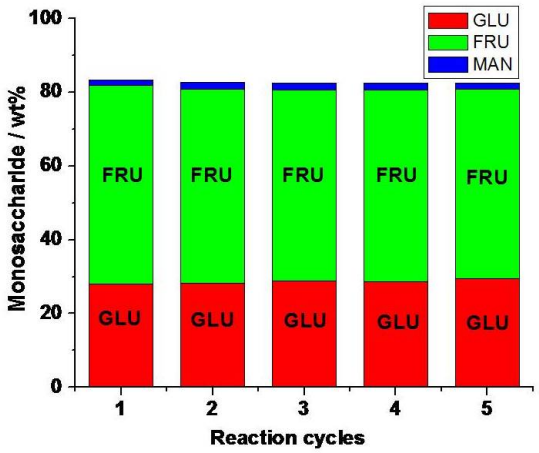


Figure S9. GLU isomerization products distribution of different reaction cycles over Sn-MWW(SP)-SSE. Reaction conditions: 1 wt% GLU (0.05 g) in ethanol (4.95 g), GLU/Sn=74, 90 °C, 8h. The fructose and mannose concentrations are obtained after the indicated reaction time and the 24 h hydrolysis. Reaction time is the time for reaction in ethanol before the addition of water. GLU, FRU and MAN stand for glucose, fructose and mannose, respectively.

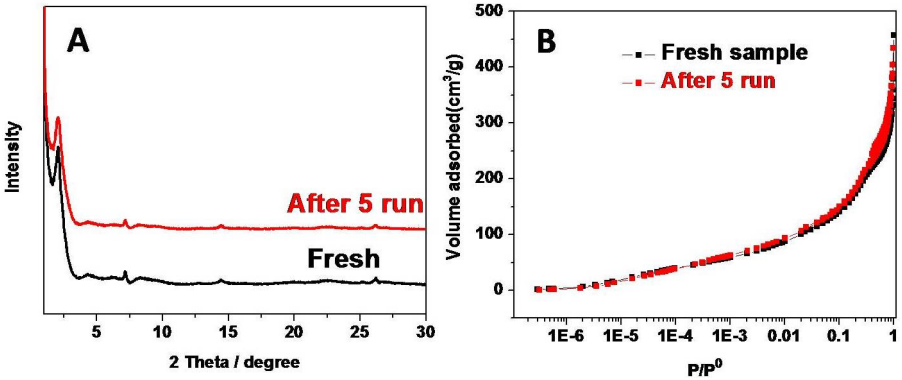
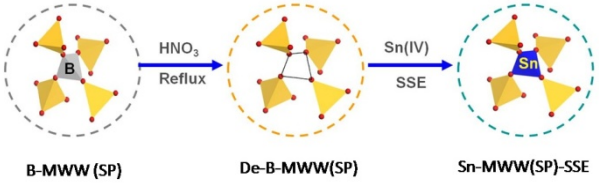
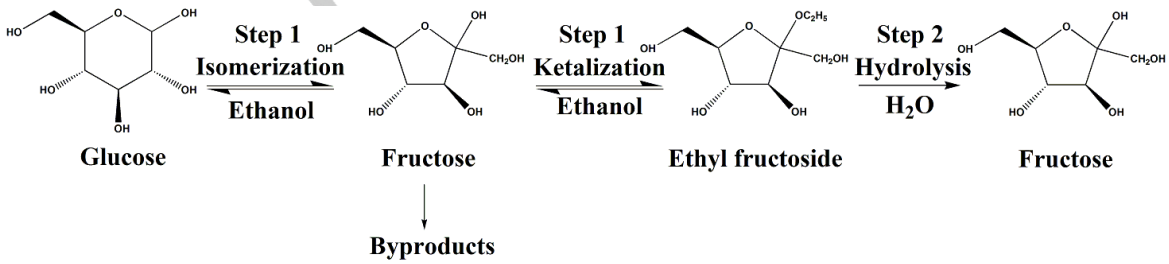


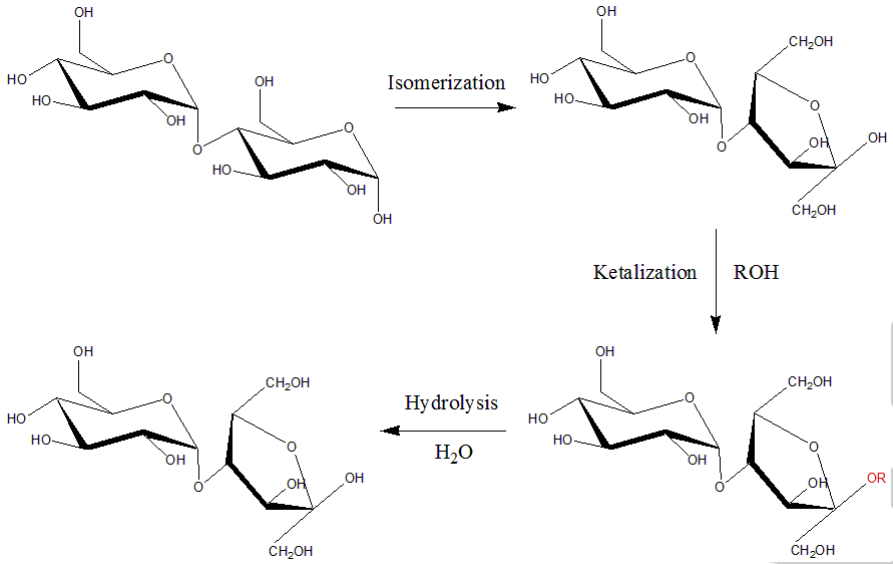
Figure S10. A). XRD patterns and B). Ar adsorption/desorption of Sn-MWW(SP)-SSE fresh sample and sample after 5 reaction cycles.



Scheme 1. Solid-state-exchange (SSE) route for inserting Sn into B-MWW(SP) after its deboronation (De-B-MWW(SP)) to obtain Sn-MWW(SP)-SSE.



Scheme S2. Reaction scheme for converting GLU to FRU in ethanol.



Scheme S3. Reaction scheme for converting MAL to MALTU in alcohols.

Table S1. B-V oxidation of 2-adamantanone reported in the literature.

Catalysts	Con. %	Selec. %	Temperature & time	Solvent	Reference
Sn-MWW	46	>98	90 °C, 4h	Chlorobenzene	Microporous Mesoporous Mater. 2013, 165, 210
Sn-MCM-56	56	>98	90 °C, 4h	Chlorobenzene	Microporous Mesoporous Mater. 2013, 165, 210
Sn-BEA	57	>98	90 °C, 2h	Chlorobenzene	Microporous Mesoporous Mater., 2013, 165, 210
Sn-BEA	64.7	>98	90 °C, 4h	Chlorobenzene	Dalton Trans. 2014, 43, 8196
Sn-BEA	85.7	>98	70 °C, 3h	Chlorobenzene	J. Phys. Chem. C 2011, 115, 3663
Sn-BEA	5.7	60	70 °C, 3h	dioxane	J. Phys. Chem. C 2011, 115, 3663
Sn-BEA	94	>98	56 °C, 6h	MTBE	Nature 2001, 423
Sn-BEA	95	>98	56 °C, 8h	MTBE	Chem. Eur. J. 2002, 8, 20, 4708
Sn-BEA	99	>98	75 °C, 16h	dioxane	ACS Catal. 2012, 2, 2695
Sn-MFI	13	95	75 °C, 16h	dioxane	ACS Catal. 2012, 2, 2695
Sn-MFI nanosheets	92	>98	75 °C, 16h	dioxane	ACS Catal. 2012, 2, 2695
Sn-DZ-1 (delaminated Sn-MWW)	99	>90	75 °C, 24h	dioxane	ACS Catal. 2015, 5, 3108

Table S2. GLU isomerization over different catalysts with conversion approximately 75%.[a]

Catalysts	Si/Sn	Time[b] /h	Conversion /%	Yield of FRU /%	FRU Selectivity /%
Sn-MWW(3D)	94	24	76.0	54.7	72.0
Sn-MWW(SP)-SSE	125	8	75.4	54.6	72.4
Sn-SPP	186	24	78.0	56.1	71.9
Sn-BEA-F	125	8	73.8	30.3	41.1

[a]), Reaction condition, 0.05 g of glucose, 4.95 g of ethanol (1 wt % glucose in ethanol solution), GLU/Sn=74, at 90 °C. After quenching the reactor in an ice bath, 6.45 g of deionized water was added to hydrolyze the ethylated sugars at 90 °C for 24 h. The fructose yields listed here are those obtained after the reaction time and the 24 h hydrolysis. [b]), Reaction time is the time for reaction in ethanol before the addition of water.

References

S1) P. Wu, T. Tatsumi, T. Komatsu, T. Yashima*, J. Phys. Chem. B* **2001**, *105*, 2897-2905.
S2) S. Maheshwari, E. Jordan, S. Kumar, F. S. Bates, R. L. Penn, D. F. Shantz, M. Tsapatsis, *J. Am. Chem. Soc.* **2008**, *130*, 1507-1516.
S3) C. Hammond, S. Conrad, I. Hermans, Angew. Chem. Int. Ed. **2012**, 51, 11736-11739.
S4) Q. Guo, F. Fan, E. A. Pidko, W. N. P. van der Graaff, Z. Feng, C. Li, E. J. M. Hensen, *ChemSusChem* **2013**, *6*, 1352-1356.
S5) A. Corma, L. T. Nemeth, M. Renz, S. Valencia, *Nature* **2002**, *412*, 423-425.
S6) N. K. Mal, V. Ramaswamy, P. R. Rajamohanan, A. V. Ramaswamy, *Microporous Mater*. **1997**, *12*, 331-340.
S7) P. I. Ravikovitch, A. V. Neimark, *Colloids Surf., A* **2001**, *187-188*, 11-21.
S8) a) F. C. Jentoft, *Adv. Catal.* **2009**, *52*, 129-211; b) S. Roy, K. Bakhmutsky, E. Mahmoud, R. F. Lobo, R. J. Gorte, *ACS Catal.* **2013**, *3*, 573-580.